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Evaluation of properties of fast pyrolysis products obtained, from Canadian waste biomass

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ABSTRACT

Pyrolysis is known as the most common method for the conversion of waste biomass such as agricultural wastes, forest residues and animal manure to value-added products such as bio-oil and bio-char. Four types of Canadian waste biomass including wheat straw, saw dust, flax straw and poultry litter, collected in Saskatchewan (Canada), were used for fast pyrolysis process using a mobile pyrolysis unit. For each biomass, pyrolysis was performed at three different temperatures (400, 475 and 550 °C) to investigate their effects on the properties of products. A comprehensive physical and chemical characterization was conducted for all biomass and pyrolysis products including bio-char, bio-oil and gas phase. Saw dust and wheat straw showed the largest cellulose and lignin contents (37.7 and 20.8 wt%, respectively). Poultry litter had the highest ash content (12.3 wt%). Amount of bio-oil collected from liquid product increased by an increase in the pyrolysis temperature for wheat straw and poultry litter. Total acid number of bio-oil product decreased by an increase in the pyrolysis temperature. Carbon content of bio-char was in the range of 70–81 wt% which was much larger than that for original biomass. The pH for bio-chars derived from the wheat straw and poultry litter was in the range of bases. For all samples, the concentrations of CH_4 and H_2 in the gas phase increased with an increase in the pyrolysis temperature.

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1. Introduction

Biomass is the world's largest and most sustainable energy resource. Estimation shows ~220 billion dry tones of annual available biomass in the world [1]. The biomass availability in Canada is around 561 million dry tones [2]. The three major components of biomass are cellulose, hemicellulose and lignin. Cellulose (25–45 wt%), is composed of monomers of glucose, a six-C sugar linked by β (1–4) glycoside bonds. Hemicellulose (20–40 wt%) is a highly branched carbohydrate and is composed of both hexose and pentose sugar. Lignin (10–30 wt%) consists of macromolecules in nature with phenolic character. It has helical structure and contains ether and carbon–carbon linkages. Lignin is a source of aromatics or valuable phenolic by-products, and combustion of lignin contributes energy [3]. The four types of feedstock used in this study including forest residue (pinewood sawdust), agricultural residue (wheat and flax straw) and poultry litter, are abundant across Saskatchewan and Canada. Forest biomass can be found from coast to coast in Canada's boreal forest and can be harvested year-round. Canada's average annual round wood cut has been estimated at 167.5 million m^3 creating over 60 million tones of residues [4,5]. These annual harvests are taken from approximately one million hectares, constituting only about 0.25% of the total forestland in Canada [4]. Therefore, more could be harvested to replace bio-fuels without exceeding Canada's sustainable forestation limits.

The potential for agricultural biomass derived energy is less than that of forest-derived biomass in Canada. Most agricultural residues have alternative uses as animal fodder or soil conditioners and typically have much lower energy intensity than wood (i.e., 1 m^3 of wood contains as much energy as 50 m^3 of baled field residues) [4]. However, agricultural residues can provide many energy benefits in a rural or localized setting. Annual production of different plant biomass used in this study was as follows for 2010 in Saskatchewan: 9.5 million tons of wheat, 1.9 million tons of barley and 0.3 million tons of flax [6,7].

World poultry farming industry is continuously growing due to the world population increase. Land application and cattle field application due to their own problems cannot be considered as the main solutions for poultry litter disposal [8,9]. Therefore, use of this biomass for pyrolysis or other thermo-chemical processes to obtain fuels and value-added products is an effective alternative.

Pyrolysis is a thermo-chemical process which simply can be defined as applying heat to degrade biomass in an inert atmosphere (absence of oxygen). It transforms unstable biomass (~17 MJ/kg)

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and other organic materials into a more stable, high-energy-density liquid known as bio-oil (~22 MJ/kg), a high-energy-density solid known as bio-char (~18 MJ/kg), and a relatively low-energy-density gas (~6 MJ/kg) [10–12]. Depending on the operating conditions, there are two common methods for pyrolysis. Slow pyrolysis which is the conventional method used with a low heating rate and fast pyrolysis. Residence time for slow pyrolysis is in the range of minutes but for fast pyrolysis is in the range of seconds. Yield of liquid product (bio-oil) is higher in the case of fast pyrolysis as compared with that for slow pyrolysis. The main interest in pyrolysis process is due to the conversion of biomass to potential fuels such as bio-oil and bio-char which can be stored or transported much easier as compared to parent biomass. In addition, bio-oil obtained from the pyrolysis process can be considered as a source of useful chemicals [13] and bio-chars can be used for soil amendment [14] or be converted to value added products such as activated carbons [15].

Mobile pyrolysis technology is an effective solution for managing agricultural wates, forest residues and livestock residues. It can simultaneously improve weak rural economies and help to mitigate the threat of global climate change. Currently, there is an increasing demand for alternative, non-edible biomass resources for the bio-energy and bio-chemical sectors. Economically, conversion of non-edible biomass to bio-products in rural areas using mobile pyrolysis unit can provide new income and employment opportunities to farmers and rural communities. Technically, this process produces bio-char which can be used for soil amendment, as bio-fertilizer or fuel. Bio-oil can be used locally as fuel or can be converted subsequently into bio-gasoline, bio-diesel or bio-chemicals.

This paper presents results of characterization for biomass feedstocks and investigates the effects of pyrolysis temperature (400, 475 and 550 °C) on the pyrolysis products (bio-oil, bio-char and gas phase) obtained by fast pyrolysis of four different types of Canadian waste biomass including wheat straw, saw dust, flax straw and poultry litter, collected in Saskatchewan (Canada). Pyrolysis process was performed in Saskatchewan Research Council (Saskatoon, Canada) using a mobile pyrolysis unit. Physical and chemical characterizations of precursors and products were performed in the Department of Chemical and Biological Engineering, University of Saskatchewan.

2. Experimental

Wheat straw, saw dust, flax straw and poultry litter collected in Saskatchewan are used as the feedstock for the pyrolysis process. Pyrolysis of these four different biomass was performed at the Saskatchewan Research Council (Saskatoon, Canada) using a mobile pyrolysis unit made by ABRI Tech Inc. (QC, Canada) at three different temperature in the range of 400–550 °C. This unit is an auger pyrolysis system with the capacity of 1 ton/day. Steel beads are used as the heat carrier without any fluidizing gas. System works under atmospheric condition. Vapor residence time is ~1 s. A blower downstream the condensation system facilitates removal of hot vapor. Bio-char residence time is ~15 min and separation of char from steel beads is simply based on density difference. To optimize the energy consumption, heat required for dryer is provided by pyrolysis gas product obtained from pyrolyzer. Pyrolysis time for each run was 8 h and an average feedrate of 200 g/min was used for these experiments.

2.1. Characterization methods

Gas samples were collected using 1-liter tedlar bags for further analysis. liquid products included two phases of organic and aqueous. Different types of solvents such as chloroform, dichloromethane and diethyl ether have been used for the separation of water from bio-oil. In this study, bio-oil was extracted using diethyl ether (equi-volume extraction) and the solvent was recovered by rota-evaporator at 25 °C [16,17]. Diethyl ether has medium polarity (2.8) and low boiling point (34.6 °C) which makes its removal easier with lower loss of light compounds from bio-oil. Solid sample was collected after pyrolysis process from the operation unit.

Bio-oil analysis: GC analysis was carried out using a Varian CP-3800 gas chromatograph equipped with a flame ionization detector (FID) and a 30 m/0.25 mm column coated with 0.25 μm film thickness (DB-5 column). Helium was used as the carrier gas at a flow rate of 1.2 mL/min at a column pressure of 22 kPa. Each sample was injected into the injection port of the GC using a split ratio of 50:1. Separation of compounds was achieved following a linear temperature program of 50–250 °C (5 °C/min) then 250 °C. The total run time was 45 min. The percentage composition was calculated using the peak normalization method. The GC/MS analysis was carried out on a Varian Saturn 2200 GC/MS fitted with the same column and a temperature program as described earlier. MS parameters: ionization voltage (EI) 70 eV, peak width 2 s, mass range 40–500 amu, and detector voltage 1.5 V. Peak identification was carried out by comparison of the mass spectra available on NIST-I and NIST-II libraries.

Determination of extractives, cellulose, hemicellulose, and lignin in biomass: Amount of extractives in biomass feedstock was determined using the extraction process in a Soxhlet extraction set-up. Hexane, ethanol and distilled water were used as solvents. Compounds such as non-polar lipids, hydrocarbons, and terpenoids were separated in the first extraction step using n-hexane. Ethanol was used for the second extraction step from the raffinate biomass to remove polar compounds such as polar waxes, sterol, and chlorophyll. Last step of extraction was performed using water for removal of compounds such as non-structural sugars from the raffinate remained from second extraction. To determine cellulose and hemicellulose contents, NREL method [18] was used. Acid hydrolysis using H_2SO_4 was used to convert these classes of chemicals to sugars. After neutralization by calcium carbonate, one Hewlett Packard liquid chromatography (HPLC) with RI detector was used for quantification of sugars. One Aminex HPX 87P column equipped with a deashing guard cartridge (BioRad) was used for analysis. The mixed sugar standards including celluboise, glucose, xylose, galactose, arabinose and mannose were used for quantification.

Dynamic viscosity measurement: Viscosities were measured at 40 °C using a Brookfield digital viscometer (DV-I).

Gas chromatography technique (for gas phase): Teddler bags were used to collect the product gas from the mobile pyrolysis unit and injected into the gas chromatograph (Agilent 7890A) equipped with two TCD (Thermal conductivity detector) and one FID (Flame ionization detector) columns.

Heating value measurement (for bio-oil and bio-char): Higher heating value (HHV) was determined in a static oxygen bomb calorimeter, a sealed Parr 1108, following the procedure described by Hubbard and Scott [19]. The sample (1.0 g) was put in a stainless steel crucible and then placed inside the bomb calorimeter. A 1.0 mL portion of water was added into the bomb, and the bomb was filled with oxygen (2 MPa pressure) at room temperature (25 °C). The calorimeter was placed in an isothermal jacket. The electrical energy (40 V) was applied for ignition using a platinum wire. The bomb calorimeter was submerged in a calorimeter cane filled with distilled water. Benzoic acid was used as standard material for calibration of bomb calorimeter.

Moisture and ash contents (for bio-char and biomass): They were determined according to ASTM D 2866-94 (Approved 1999). 5.0 g of sample was placed on a crucible and was dried to constant weight

Table 1
Concentrations of three extracts (hexane, ethanol and water) as well as cellulose, hemicellulose, and lignin concentrations in four biomass feedstocks on ash-free basis.

Extractives	Flax straw (wt%)	Wheat straw (wt%)	Saw dust (wt%)	Poultry litter (wt%)
Hexane extract	2.2 ± 0.1	1.9 ± 0.1	2.9 ± 0.1	2.8 ± 0.1
Ethanol extract	7.9 ± 0.2	2.1 ± 0.2	7.0 ± 0.2	5.5 ± 0.3
Water extract	10.0 ± 0.3	10.1 ± 0.3	5.1 ± 0.3	8.6 ± 0.4
Cellulose	32.3 ± 0.2	35.4 ± 0.2	37.7 ± 0.2	n/a
Hemicellulose	27.5 ± 0.3	29.7 ± 0.3	31.4 ± 0.3	n/a
Lignin	20.1 ± 0.3	20.8 ± 0.3	15.9 ± 0.3	n/a

at 150 ± 5 °C (for 3 h) for moisture analysis, then, the crucible was placed in a muffle furnace having air circulation at 650 ± 25 °C for 3 h. Ashing was considered complete when constant weight was achieved.

Moisture content measurement (for bio-oil): The moisture content of the bio-oil was measured by the Karl-Fischer titrator. The Karl-Fischer titration was carried out by Mettler Toledo Titrator DL32, Provided by Mettler Toledo, USA. Sample (0.1 g) was injected into the titration cell (Anolyte) connected to a balance to measure the amount of sample injected. Anolyte was provided by Fluka (Germany). Samples with water content more than 5 wt% were diluted with methanol before injection. Iodine produced by iodide available in the Anolyte reacts with water. As soon as all the water reacted, the free iodine was detected in the Anolyte and the Karl-Fischer titration was terminated [20].

Particle size analysis (for bio-chars): Particle size distribution (PSD) of bio-chars was determined based on the laser beam diffraction pattern of particles, by the Malvern Mastersizer S Long Bench Particle Size Analyzer (Malvern instruments Ltd., Malvern, UK) using wet method. The accuracy of the measurements was ±2%.

Particle size analysis (for biomass): Approximately 200 g of biomass was loaded into the stack of tray sieves. The stack included 5 sieves and was placed in a hammer shaker. The hammer shaker was run for 5 min.

pH measurement (for bio-char): pH of samples was determined according to ASTM D 3838-80 (Approved 1999).

Porous characteristics measurement: BET (Brunauer, Emmett, and Teller) surface area and total pore volume of bio-chars were determined by an automated gas adsorption analyzer, ASAP 2020 (Micromeritics, Instruments Inc., GA USA). After degassing of samples at 300 °C to a vacuum of 550 μmHg, nitrogen adsorption–desorption isotherms at −196 °C were measured by this equipment. The BET surface area was calculated by using the BET equation [21]. For each analysis ~0.2 g of sample was used. The accuracy of measurements performed by this equipment was ±5%.

Raman spectroscopy: Raman Spectroscopy of bio-char samples was performed using a Renishaw inVia Raman microscope equipped with 514 nm laser for the Raman shift of 400–3200 cm^{-1}. 10% laser power was used with 10 s of exposure time and a total of 10 acquisitions were collected.

Total acid number (TAN) measurement (for bio-oil): Total acid number of samples was determined according to ASTM D D664-09a which is expressed as milligram of potassium hydroxide per gram of sample, that is required to titrate a sample in a mixture of toluene and propan-2-ol to which a small amount of water is added. For titration, a 0.1-mol/L alcoholic KOH solution (in propan-2-ol) is used. 0.10–0.25 g of sample was used for the titration. Titration was performed using two electrodes which one of them was a reference electrode (Ag/AgCl).

Ultimate (CHNS) analysis: Carbon, hydrogen, nitrogen, and sulphur percentages were measured by Elementar Vario EL III. Through quantitative high temperature decomposition, solid substances are changed into gaseous combinations. 0.1 g sample was burned at 1000 °C and the released gases were separated into their components.

Volatile matter: The volatile matter in the biomass was determined by the procedure given in ASTM D 3175-07. The biomass sample (1.0 g) was taken and placed in muffle furnace maintained at 950 ± 10 °C for 7 min. Then, the crucible was removed from the furnace and placed in the desiccators. The loss of weight was measured as the volatile matter in the biomass.

3. Results and discussions

3.1. Biomass (feedstocks) characterization

Some compounds present in biomass such as lipids, chlorophyll, wax, inorganic materials, and non-structural sugars can interfere with later analytical and analysis steps of biomass [18]. These compounds are removed from biomass feedstocks using hexane, ethanol and water extractions. Table 1 shows the concentrations of three extract phases (hexane, ethanol and water) for all precursors as well as cellulose, hemicellulose and lignin in the agricultural waste and forest residues used in this study. Hexane extractives were the smallest portion of extractives for all biomass feedstocks. The polar compounds extracted were more for flax straw and saw dust. Wheat and flax straw showed more water soluble extracts. Flax straw had the maximum total amount of extractives (20.1 wt%) whereas wheat straw gave the lowest amount (14.1 wt%).

Cellulose, hemicellulos, and lignin are three major components which form biomass besides some extractives, ash, and protein [22,23]. In case of saw dust, it is surprising that the lignin content was not larger than that in other feedstocks (see Table 1), as wood has strong and rigid plant structure. The lignin content of softwoods is generally in the range of 16–33 wt% [5] and was found ~16 wt% for saw dust in this work. The hemicellulose and lignin contents for wheat straw are larger and smaller, respectively, than those compared in the work by DEFRA [24], but cellulose content is in the same range (33.2 wt%). However, these results for flax straw and wheat straw comply with those obtained by Naik et al. [25].

Table 2 presents results for proximate analysis of biomass feedstocks used for this study. It is interesting that moisture content of the wood (6.2 wt%) is lower than that for agricultural residues. It has

Table 2
Proximate analysis of biomass feedstocks.

	Flax straw (wt%)	Wheat straw (wt%)	Saw dust (wt%)	Poultry litter (wt%)
Moisture content	8.1 ± 0.2	6.3 ± 0.2	6.2 ± 0.2	10.2 ± 0.5
Ash content	3.1 ± 0.2	1.3 ± 0.2	1.4 ± 0.2	12.3 ± 0.5
Volatile matter	79.9 ± 0.2	78.4 ± 0.2	81.7 ± 0.2	68.4 ± 0.3
Fixed carbon[a]	8.9 ± 0.1	14.0 ± 0.1	10.7 ± 0.1	9.0 ± 0.2

[a] Fixed carbon is calculated by difference.

Table 3
Elemental analysis of biomass feedstocks on ash-free basis.

Element	Flax straw (wt%)	Wheat straw (wt%)	Saw dust (wt%)	Poultry litter (wt%)
C	47.8 ± 0.2	45.4 ± 0.2	45.2 ± 0.2	50.6 ± 0.8
H	6.4 ± 0.1	6.2 ± 0.1	6.7 ± 0.1	6.5 ± 0.1
N	0.07 ± 0.01	0.12 ± 0.02	0.01	4.4 ± 0.1
S	0.01	0.02	0.01	0.50
O[a]	45.7 ± 0.2	48.3 ± 0.2	48.0 ± 0.2	37.9 ± 0.9

[a] Oxygen is calculated by difference.

been reported that agricultural residues tend to have lower moisture contents [26,27]. The low moisture content observed for the mixed wood could be due to air drying the wood experienced over time, transportation, etc. As it can be seen in this Table, the poultry litter possessed the highest ash content (12.3 wt%). The large amount of volatile matter present in saw dust, flax straw and wheat straw shows that these precursors have potential for production of porous material such as activated carbon and carbon sorbents using pyrolysis followed by activation processes [28] as compared with poultry litter. In addition, considering the fact that ash content will not participate in pyrolysis and activation processes, the larger amount of ash content for poultry litter which increases approximately linearly by burn-off degree in pyrolysis and activation processes shows that this precursor is not suitable for the production of porous value-added products, but it can be seen later in this paper that this char can be suitable for soil amendment and increase in the crop yield.

Table 3 shows the elemental (C, H, N, S and O) analysis of biomass feedstocks. The elemental analysis result for wheat straw is in good agreement with the work done on the wheat straw by Greenhalf et al. [29]. Highest nitrogen content in this Table belongs to poultry litter, 3.9 wt%, among different types of biomass studied in this work. Poultry litter showed larger carbon content and smaller oxygen content as compared with the other feedstocks. There was no significant difference in elements' percentage for other three precursors. The source of nitrogen in agricultural and forest biomass is mainly due to their protein content.

Heating values for biomass feedstocks measured by bomb calorimeter were 17.2 ± 0.2, 19.8 ± 0.2, 19.5 ± 0.2 and 23.2 ± 0.2 MJ/kg for flax straw, wheat straw, saw dust and poultry litter, respectively. These low heating values were expected for these biomass feedstocks based on the large oxygen content observed in Table 3. For first three biomass, the ash content is inversely correlated with the heating value (Table 2). In case of poultry litter, its heating value is estimated in the range of low-rank coal [30]. However, this value for poultry litter was slightly less than that (26–29 MJ/kg) reported by Agblevor et al. [31]. It can be due to the nature of poultry litter sample analyzed which is possibly a mixture of this and bedding material. Random sampling from the poultry litter showed that bedding material is accounted for 20–27 wt% of poultry litter feedstock.

Fig. 1 shows the particle size distribution for biomass feedstocks. The particle size analysis shows that poultry litter was the finest sample followed by flax straw. Saw dust had the largest particles among all biomass feedstocks.

Cellulose, hemicellulose and lignin are the main components present in biomass which are thermally decomposed and depolymerized under pyrolysis conditions. The results related to bio-char, bio-oil, and gases as the pyrolysis products and their physical and chemical characterization are discussed in the following sections.

3.2. *Bio-char characterization*

Bio-char as the solid product of pyrolysis is used for wide range of applications such as fuel, adsorbent and production of value-added products. Table 4 shows the proximate analysis of bio-chars produced at three pyrolysis temperatures (400, 475, and 550 °C) from different types of biomass. From fuel applications point of view, an increase in ash content will decrease energy density of bio-char [32] and large concentrations of alkaline and alkaline earth metallic (AAEM) species such as calcium, potassium, and sodium in bio-char and biomass, which are present in ash, result in problems in combustion processes [33]. In case of bio-char applications for production of activated carbons, in general, ash does not participate in activation process resulting in less porosity development for activated carbon products. In Table 4, as expected, ash content of the bio-char for each type of biomass increased by an increase in the pyrolysis temperature due to the higher removal of other species from the precursors at more severe conditions. Comparison of level of ash contents for bio-chars produced from different biomass with the ash contents shown in Table 2, shows that biomass with higher ash content produces bio-chars with higher level of ash content. Ash does not participate in the pyrolysis process and remains in the bio-char structure left after process. The range of ash content for bio-chars obtained from poultry litter is in agreement with the values reported by Agblevor et al. [31].

Table 5 shows the ultimate (elemental) analysis of bio-chars. The carbon content for all bio-chars is in the range of 69–83 wt%,

Table 4
Proximate analysis of bio-chars produced at different pyrolysis temperatures from four types of biomass.

	Pyrolysis temperature (°C)	Moisture content (wt%)	Ash content (wt%)	Volatile matter (wt%)	Fixed carbon (wt%)
Bio-char produced from wheat straw	400	1.97 ± 0.21	5.20 ± 0.31	36.27 ± 0.62	56.56 ± 0.38
	475	6.18 ± 0.35	7.35 ± 0.66	22.50 ± 0.26	63.97 ± 0.26
	550	6.31 ± 0.19	8.28 ± 0.17	18.62 ± 0.44	69.03 ± 0.59
Bio-char produced from saw dust	400	3.01 ± 0.41	1.82 ± 0.16	42.32 ± 0.91	52.85 ± 0.96
	475	4.02 ± 0.50	3.13 ± 0.33	27.69 ± 0.25	65.16 ± 0.24
	550	7.85 ± 0.51	3.99 ± 0.17	20.86 ± 0.64	72.43 ± 0.51
Bio-char produced from poultry litter	400	2.31 ± 0.23	33.28 ± 0.95	36.95 ± 0.71	25.62 ± 0.38
	475	1.16 ± 0.34	40.46 ± 1.68	29.16 ± 0.38	29.21 ± 0.61
	550	1.70 ± 0.22	46.31 ± 1.72	20.35 ± 0.47	31.64 ± 0.47
Bio-char produced from flax straw	400	8.30 ± 0.67	8.93 ± 0.81	38.09 ± 0.58	48.39 ± 0.67
	475	3.51 ± 0.46	9.36 ± 0.73	31.28 ± 0.61	55.85 ± 0.55
	550	5.67 ± 0.49	10.64 ± 0.37	19.42 ± 0.42	64.27 ± 0.41

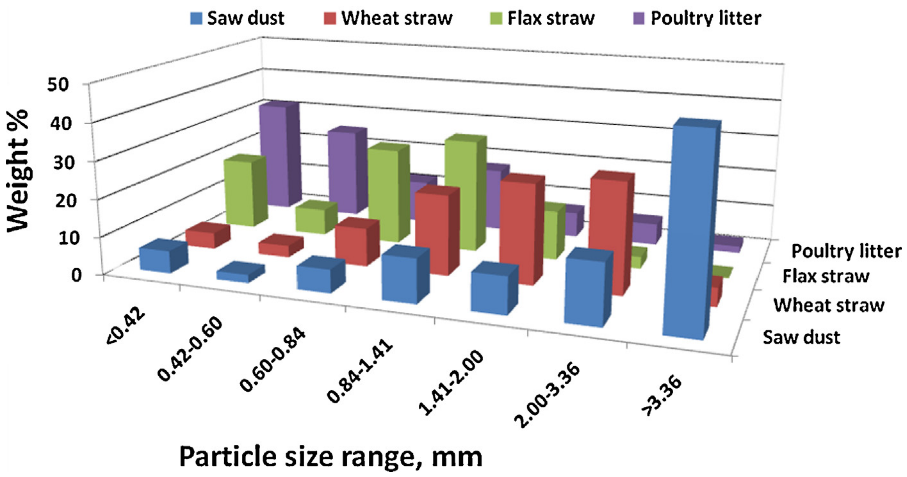

Fig. 1. Particle size distribution for biomass feedstocks.

while the carbon contents of the original biomass materials are in the range of 44–47 wt% (See Table 3). This large carbon content of bio-char shows its potential for being used as fuel or activated carbon precursor [34]. As expected, the nitrogen content for bio-chars obtained from poultry litter was larger than those produced from other feedstocks due to its larger nitrogen content (3.9 wt%). Large values of nitrogen content and ash content for bio-chars obtained from poultry litter show that they can be used as fertilizer to improve soil quality and crop yield. Hydrogen contents were in the range of 3–6 wt% and oxygen content decreased by an increase in the pyrolysis temperature. Carbon content showed the reverse trend. This Table also shows that decrease in atomic O/C and H/C ratios by an increase in pyrolysis temperature as a general trend which helps to increase energy density and decrease water vapor and smoke in bio-char combustion [35] due to highly carbonaceous structure of bio-char, especially at larger pyrolysis temperatures [36]. Using data presented in this Table, empirical formula for bio-chars can be calculated. For example, the empirical formulas for bio-char and bio-oil collected from the pyrolysis of saw dust at 550 °C, respectively, are as follows: $CN_{0.01}H_{0.53}O_{0.14}$ and $CN_{0.01}H_{1.10}O_{0.23}$. It shows that the percentages of hydrogen and oxygen are decreased and carbon percentage has increased in the bio-char compared with those in bio-oil obtained from saw dust at 550 °C.

The heating value for wheat straw, saw dust, poultry litter, and flax straw were 19.8, 19.5, 23.2 and 17.2 MJ/kg, respectively. Table 6 presents the heating value and acidity of bio-chars produced from different biomass at different pyrolysis temperatures. For bio-chars produced from wheat straw and flax straw, the heating value increased by an increase in the pyrolysis temperature. This maybe due to a decrease in the oxygen content by pyrolysis temperature (See Table 5), while for bio-chars from other biomass, no trend was observed. The heating value of bio-chars was larger than that for all feedstocks except poultry litter due to low O/C and H/C ratios for bio-chars comparing with those for biomass (see Table 5) and lower heating content of C—O and C—H bonds comparing to that for C—C bond [37]. Reverse trend for poultry litter can be due to large percentage of bedding material content in poultry litter. This bedding material is made of hardwood shavings.

As it can be seen in Table 6, bio-chars produced from the saw dust showed pH in acidic range (4.4–5.1). The pH for bio-chars derived from the wheat straw and poultry litter were in the range for bases. The value of pH for bio-chars derived from poultry litter is in agreement with that measured by Chan et al. [38] who produced the bio-char at 450 °C. In addition, Song and Guo observed similar trend of increase in pH with an increase in pyrolysis temperature [39]. Bio-char can be used in soil to increase the crop yield and for soil amendment due to its high nitrogen content [40] and its more stability as compared with the original biomass [41]. Also, bio-char samples produced from poultry litter have shown their potential in pot trial for soil amendment [42].

Porous characteristics including BET (Brunauer, Emmett and Teller) surface area and total pore volume were measured for bio-chars. BET surface area for all bio-chars was less than 5 m^2/g and total pore volumes were <0.005 cc/g. The small values of these porous characteristics show that char has a rudimentary porous

Table 5
Ultimate (CHNS) analysis of bio-chars obtained at different pyrolysis temperatures from four types of biomass on dry and ash-free basis.

	Pyrolysis temperature (°C)	N (wt%)	C (wt%)	S (wt%)	H (wt%)	O[a] (wt%)	H/C	O/C
Bio-char produced from wheat straw	400	0.59 ± 0.02	71.28 ± 0.53	0.55 ± 0.09	4.85 ± 0.26	22.73	0.82	0.24
	475	0.55 ± 0.01	74.86 ± 0.03	0.13 ± 0.02	3.92 ± 0.02	20.54	0.63	0.21
	550	0.61 ± 0.17	83.10 ± 0.18	0.17 ± 0.04	3.22 ± 0.10	12.90	0.46	0.12
Bio-char produced from saw dust	400	0.05	71.50 ± 0.20	0.17 ± 0.02	4.72 ± 0.15	23.56	0.79	0.25
	475	0.14 ± 0.01	80.39 ± 0.07	0.00	3.81 ± 0.01	15.66	0.57	0.15
	550	0.17 ± 0.01	81.32 ± 0.91	0.01	3.57 ± 0.01	14.92	0.53	0.14
Bio-char produced from poultry litter	400	9.99 ± 0.10	69.17 ± 0.79	2.00 ± 0.02	5.83 ± 0.06	13.01	1.01	0.14
	475	9.06 ± 0.06	77.14 ± 0.51	2.79 ± 0.13	4.74 ± 0.05	6.27	0.43	0.06
	550	8.36 ± 0.01	83.03 ± 0.72	2.88 ± 0.07	4.22 ± 0.03	1.50	0.42	0.01
Bio-char produced from flax straw	400	1.16 ± 0.02	71.15 ± 0.15	0.09	5.02 ± 0.10	22.58	0.85	0.24
	475	1.02 ± 0.02	76.61 ± 0.02	0.00	4.37 ± 0.01	18.00	0.68	0.18
	550	0.98 ± 0.01	82.56 ± 0.07	0.02	3.72 ± 0.08	12.71	0.54	0.12

[a] Oxygen content is calculated by difference.

Table 6
Heating value and pH measurements for bio-chars obtained at different pyrolysis temperatures from four types of biomass.

Feed	Temperature (°C)	Heating value* (MJ/kg)	pH*
Bio-char derived from wheat straw	400	21.9	7.8
	475	25.2	9.5
	550	25.8	9.6
Bio-char derived from saw dust	400	24.4	4.4
	475	28.6	4.8
	550	26.0	5.1
Bio-char derived from flax straw	400	21.8	6.0
	475	26.3	7.2
	550	30.1	8.0
Bio-char derived from poultry litter	400	23.9	7.8
	475	18.9	9.4
	550	18.7	9.5

* Error margins for the heating value and pH measurements were ±0.7 MJ/kg and ±0.1, respectively.

structure. The porous characteristics of these bio-chars can be improved using physical and chemical activation processes [15].

To study and compare the typical structure of bio-chars as a carbon-based material with well-known carbon material such as graphite, Raman analysis was performed for bio-chars prepared at 475 °C from four types of biomass. The spectra for this Raman analysis are shown in Fig. 2. The structure of bio-chars is clearly different from structured carbon materials such as graphite due to the presence of oxygen and different types of aliphatic groups in their structures [43]. The two relatively main broad peaks observed for all bio-chars produced in this study are as follows: a) 1520–1620 cm^{-1} (G peak) and b) 1350–1460 cm^{-1} (D peak). D band shows the presence of medium to large aromatic rings including 6 or more fused rings and presents graphitic lattice with an orderless arrangement for layers [44–46]. It shows C—C band between aromatic rings and aromatics [46]. G band shows the presence of graphitic bands, ideal graphitic lattice [45,46], and can be assigned as alkene C=C (aromatic ring quadrant breathing) [46]. As expected, these two bands for bio-chars are broader compared to sharp and distinct peak for carbon material with regular structure as that of graphite [47,48].

Particle size of bio-char is one of the parameters to influence the bio-char performance for soil amendment [49]. Fig. 3 shows the particle size distribution of bio-chars produced at pyrolysis temperature of 475 °C from different precursors. It categorizes the particles in three groups according to their size. D(v,10%), D(v,50%) and D(v,90%) values represent particle sizes which 10, 50, and 90 volume percentage of particles are smaller than those, respectively. It shows that bio-char obtained from wheat straw is finer than others and is followed by that from sawdust. It is interesting due to the fact that these biomass feedstocks were larger than the others. Bio-char prepared from poultry litter which was the finest precursor resulted in the bio-chars with largest particle size. Finer particles can provide more surface area for exchanging nutrients and water with soil in agricultural applications. However, only field test can evaluate the actual performance of particles with different size ranges.

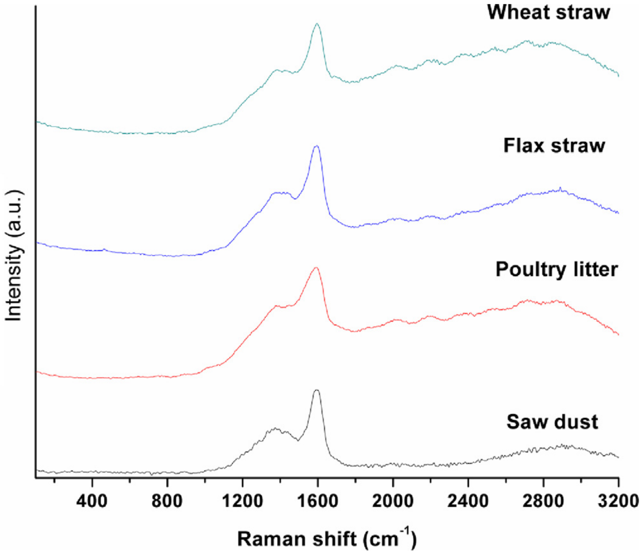

Fig. 2. Raman spectra for bio-chars produced from four types of biomass at 475 °C.

3.3. Bio-oil characterization

Bio-oil was separated from the pyrolysis liquid product using solvent extraction. Table 7 shows the yield of bio-oil collected from liquid product for each precursor. The bio-oil yield increased by an increase in the pyrolysis temperature for wheat straw and poultry litter, but not for flax straw and saw dust. The water content of organic phase of liquid product collected from pyrolysis process (not shown in this Table) was in the range of 13–38 wt% for different precursors and temperatures. In addition, Table 7 shows bio-oil yield collected from liquid product, their total acid number, heating values, viscosity (at 40 °C), and density (at 25 °C). The acid numbers are much larger than that of petroleum indicating their corrosive effect during further processing in refinery. Therefore, for using as a petroleum refinery feedstock, these raw bio-oils need further upgrading processes [50]. Lower acidity for organic phase collected from poultry litter as compared with that from the other biomass can be due to basic character of decomposition products of proteins

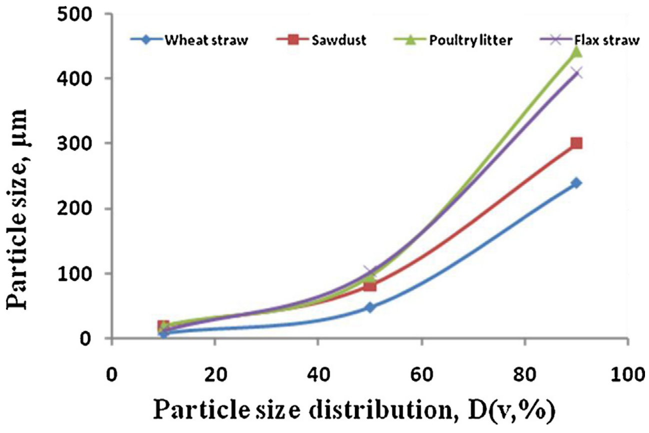

Fig. 3. Particle size distribution for bio-char produced from biomass feedstocks at pyrolysis temperature of 400 °C.

Table 7
Bio-oil collected from liquid product, total acid number, heating value, viscosity (at 40 °C), and density (at 25 °C) of bio-oil collected from pyrolysis of four types of biomass at three pyrolysis temperatures.

Feedstock for pyrolysis	Pyrolysis temp. (°C)	Bio-oil collected from liquid product (wt%)	Total acid number[a] (mg KOH/g of sample)	Heating value[a] (MJ/kg)	Viscosity[b] (cP)	Density[a] (g/cm^3)
Wheat straw	400	9.2	109.3	26.8	169	1.157
	475	19.2	92.3	22.6	147	1.033
	550	43.5	47.1	29.1	133	1.024
Saw dust	400	28.0	146.6	24.9	24	1.239
	475	52.0	117.4	23.9	43	1.156
	550	44.5	61.9	28.8	63	1.099
Flax straw	400	34.8	100.8	27.3	130	0.923
	475	41.9	93.8	29.9	173	1.050
	550	28.7	18.8	29.9	323	1.142
Poultry litter	400	26.5	69.8	31.8	418	0.910
	475	30.8	61.9	34.0	–	1.076
	550	48.0	38.3	20.5	–	1.114

[a] Error margins for total acid number, heating value, and density were ±2.1 mg KOH/g of sample, ±0.9 MJ/kg, and ±0.07 kg/m^3.
[b] After three repeats for each sample, maximum error margin of 8% was observed.

available in poultry litter [51]. Viscosity of some samples obtained from poultry litter could not be calculated due to their high viscosity at 40 °C. For saw dust and flax straw, viscosity increased by an increase in pyrolysis temperature. The viscosity of organic phase samples especially for wheat straw, poultry litter, and flax straw was much larger than that for crude petroleum (∼ 23 cP) which shows that further upgrading process is required for these bio-oils before using as fuel in engines. The large viscosity is due to the lignin-based chemicals present in organic phase with large molecular weight [52]. Heating value of organic phases is much less than that of crude oil (∼ 40 MJ/kg) which is expected due to large oxygen content for these oil phases. No trend is observed for densities of samples obtained at various pyrolysis temperatures. The density of organic phase is larger than that for no. 2 fuel oil (0.876 g/cm^3) [53] and is not far from fossil oil density range (0.75–1.00 g/cm^3) [54].

Table 8 shows the elemental (CHNS) analysis of bio-oil collected from pyrolysis liquid product. This Table shows that carbon and hydrogen content of bio-oils are larger than those for feedstock and oxygen content is lower (Table 3). In Table 3, the total percentage for carbon and hydrogen for all precursors is in the range of 51–57 wt%, but that for bio-oil phase is in the range of 69–83 wt% (Table 9). It clearly shows larger energy density of bio-oil as compared with that for biomass precursor. Nitrogen content of organic phase is larger than that for precursor and bio-char for all biomass which shows that nitrogen mostly remains in the liquid products during pyrolysis process. Although oxygen content for each bio-oil is much less than that for biomass precursor, it is still large and needs to be reduced by methods such as hydrotreating to obtain suitable transportation fuel. Low sulphur content of organic phase is one of the advantages of bio-oil for fuel applications. Empirical formulas for each bio-oil phase can be developed using the results in Table 8. For example, the empirical formulas for organic phase of bio-oils obtained from saw dust at 400, 475 and 550 °C are as follows: $CN_{0.01}H_{1.24}O_{0.34}$, $CN_{0.01}H_{1.06}O_{0.28}$ and $CN_{0.01}H_{1.10}O_{0.23}$

It shows that largest H/C ratio belongs to bio-oil prepared at 400 °C which is still smaller than that for conventional heavy and light crude oils (1.5–1.7). This ratio should increase to values in the range of 1.9–2.0 for transportation fuels. Upgrading processes such as hydrotreating help to increase this ratio by hydrogen addition. Large oxygen content of bio-oil, as seen in elemental analysis results (Table 8), is a drawback for bio-oil and decreases heating value and stability of bio-oil. The empirical formulas show that although bio-oil prepared at 400 °C has the largest H/C ratio, its O/C ratio is higher than those in other saw dust derived bio-oils. hydro-deoxygenation process is needed for oxygen removal and increases hydrogen content at the same time. These formulas and elemental analysis can be used for preliminary evaluation of upgrading cost required for each bio-oil through simple estimation for items such as hydrogen required for upgrading processes.

Table 9 identifies and quantifies the chemicals produced from various bio-oils. The bio-oil product is mostly formed and dominated by oxygenated compounds. The main compounds present in the bio-oil were phenolic compounds, benzaldehydes, aldehydes, benzoicacids, benzenediols, naphthalene and indoles. The oil obtained from poultry litter contains nitrogen compounds also. These compounds include pyridine, pyrazine and indolizine. Chemicals such as naphtho thiophene, cyclo pentane and cycloctateraene are categorized under other compounds category. Hence, the data indicate that bio-oil can be used as source of chemical feedstocks and fuel [5]. Phenols are used in the production of resins and phenolic derivatives can be used as flavors in the food industry [55].

3.4. Gas phase analysis

Figs. 4–7 show the gas phase composition measured by gas chromatography for gases produced from flax straw, saw dust, poultry litter and wheat straw, respectively. The gas product mostly included CO_2, CO, H_2 and CH_4. In addition, small amount of light hydrocarbons (mostly C_2 and C_3) is produced during pyrolysis. Pyrolysis of saw dust at 550 °C showed the highest H_2 concentration (16.9 mol%), while the largest CO concentration (39.5 mol%) was for saw dust pyrolyzed at 400 °C. For all samples, the concentrations of CH_4 and H_2 increased with an increase in the pyrolysis temperature. Increase in H_2 production is due to more severe cracking of hydrocarbons at higher temperatures [56,57]. Increase in CH_4 yield can be a result of lignin decomposition at higher temperatures [58] because lignin's contribution in CH_4 production is more than that from cellulose and hemicellulose which in fact increases by increase in pyrolysis temperature up to 500 °C [59]. Lignin has also major contribution for H_2 production [60]. As a general trend, hemicellulose and cellulose have the main contribution in the production of CO_2 and CO, respectively. An increase in the pyrolysis temperature for all feedstocks resulted in the decrease of CO_2 concentration. The only exception for this trend is concentrations of CO_2 for wheat straw sample pyrolyzed at 475 and 550 °C. Formation of CO_2 at lower temperatures is mostly due to the decomposition of hemicellulose, but at higher temperature there can be small contribution of lignin

Table 8
Elemental (CHNS) analysis of organic phase collected from bio-oils produced from four types of biomass at three pyrolysis temperatures.

Feedstock for pyrolysis	Pyrolysis temp. (°C)	N (wt%)	C (wt%)	S (wt%)	H (wt%)	O[a] (wt%)
Wheat straw	400	0.46 ± 0.09	60.6 ± 0.11	0.01	13.05 ± 0.42	25.84
	475	0.57 ± 0.08	61.18 ± 0.04	0.01	12.75 ± 0.60	25.47
	550	1.28 ± 0.01	61.66 ± 1.04	0.03	10.54 ± 0.37	26.45
Saw dust	400	0.76 ± 0.11	63.46 ± 0.18	0.00	6.56 ± 0.41	29.22
	475	0.42 ± 0.03	68.29 ± 0.11	0.03	6.05 ± 0.29	25.21
	550	0.57 ± 0.06	70.81 ± 0.24	0.21 ± 0.04	6.48 ± 0.17	21.93
Poultry litter	400	6.20 ± 0.12	73.18 ± 0.27	0.3 ± 0.05	10.62 ± 0.81	9.70
	475	8.58 ± 0.35	71.04 ± 0.11	0.08	9.01 ± 0.33	11.29
	550	9.77 ± 0.69	68.31 ± 0.34	0.31 ± 0.03	11.05 ± 0.67	10.56
Flax straw	400	1.54 ± 0.01	72.11 ± 0.01	0.10	7.38 ± 0.35	18.87
	475	2.02 ± 0.10	73.15 ± 0.07	0.00	7.52 ± 0.08	17.31
	550	2.87 ± 0.09	76.14 ± 0.05	0.13 ± 0.02	6.80 ± 0.35	14.06

[a] Oxygen content is calculated by difference.

Table 9
Identification and quantification of chemicals in the bio-oils produced from four types of biomass at three pyrolysis temperatures.

Samples	Wheat straw			Saw dust			Poultry litter			Flax straw		
Pyrolysis temp. (°C)	400	475	550	400	475	550	400	475	550	400	475	550
Phenols (wt%)	38.6	23.5	13.0	18.8	11.3	29.3	17.9	12.5	14.7	52.4	47.1	62.6
Ketones (wt%)	11.0	7.8	1.2	13.3	6.1	0.0	0.0	0.0	0.0	0.9	5.6	9.9
Alcohols (wt%)	0.0	5.9	0.0	0.0	3.5	2.7	6.2	6.7	4.5	2.0	2.1	3.3
Acids (wt%)	0.0	0.0	2.8	9.0	0.6	0.0	0.0	3.0	3.7	1.7	0.0	0.0
Aldehydes (wt%)	4.7	12.1	5.5	0.0	5.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0
N compounds (wt%)	0.0	0.0	0.0	0.0	0.0	0.0	35.8	12.2	13.6	0.0	0.0	0.0
Other compounds (wt%)	0.0	0.0	0.0	3.0	3.9	12.4	0.0	0.0	0.0	0.0	6.5	1.4
Identified compounds (wt%)	54.3	49.3	22.5	44.1	31.0	44.4	60.0	33.4	36.6	57.0	61.2	77.2

decomposition. Similar trend was observed by Uzun et al. [58]. During the primary decomposition of biomass which happens at lower temperatures (<500 °C), gas phase is mainly formed by CO_2 and CO. However, secondary reactions at higher temperatures are the main reasons for effective changes in the concentration of CH_4 and H_2 [61]. Therefore, as it can be seen in Figs. 4–7, H_2 concentration is much lower than that for CO, especially for temperature range of 400–475 °C. Small amounts of light hydrocarbons such as ethane, ethylene, propane and acetylene were observed in the gas product of pyrolysis process for all types of biomass except poultry litter.

The lower heating values (LHV) of the gas product collected in each run of pyrolysis process are estimated using the following equation [62] and are shown in Fig. 8:

$$\mathrm{LHV}\ (\mathrm{kJ/m^3}) = (30.0 * \mathrm{CO} + 25.7 * \mathrm{H_2} + 85.4 * \mathrm{CH_4} + 151.3 * \mathrm{CnHm}) * 4.2 \qquad (1)$$

where CO, H_2, CH_4 and CnHm are the molar concentrations of the gas components.

As it can be seen in Fig. 8, gas products obtained by pyrolysis of saw dust and poultry litter have shown largest and smallest LHV at all temperatures, respectively. In addition, LHV increased by an increase in pyrolysis temperature which is expected due to increase of H_2 and CH_4 concentrations by pyrolysis temperature, as described earlier in this section.

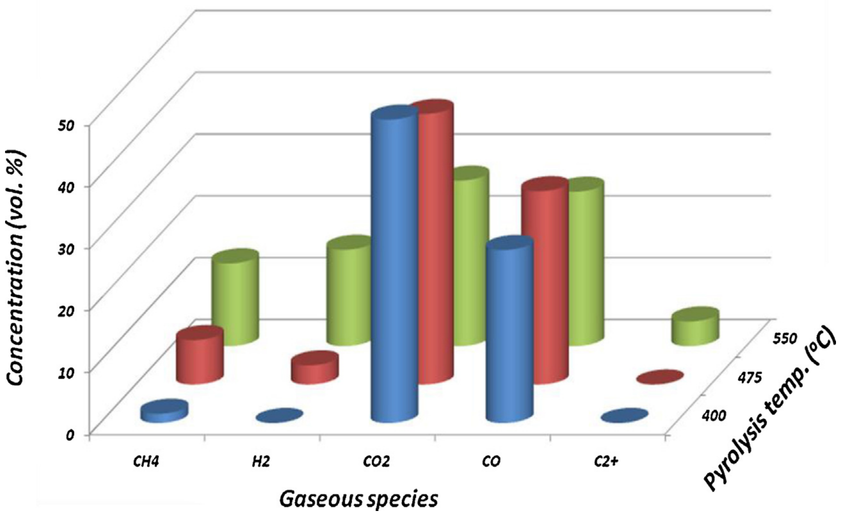

Fig. 4. Composition of gas product obtained from flax straw at three different pyrolysis temperatures.

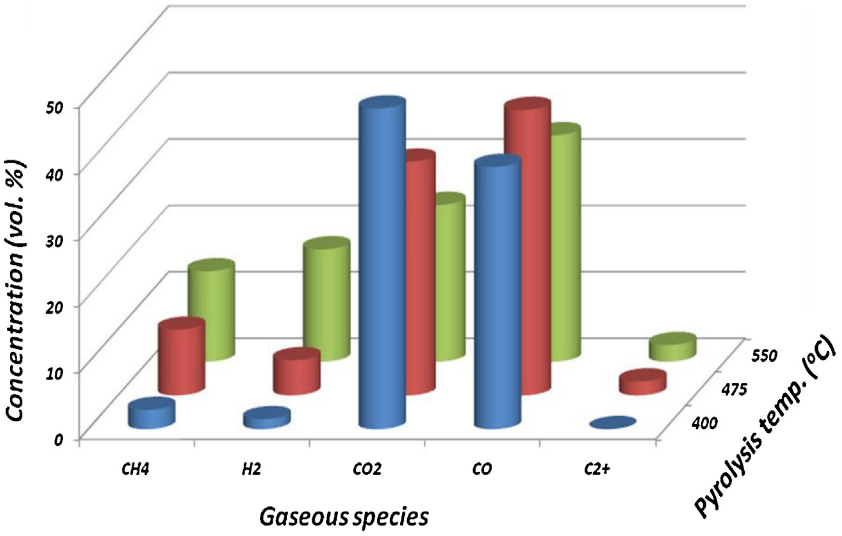

Fig. 5. Composition of gas product obtained from saw dust at three different pyrolysis temperatures.

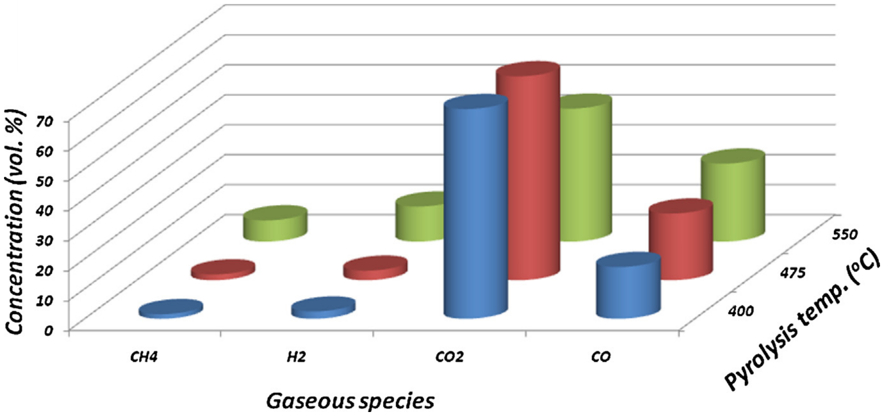

Fig. 6. Composition of gas product obtained from poultry litter at three different pyrolysis temperatures.

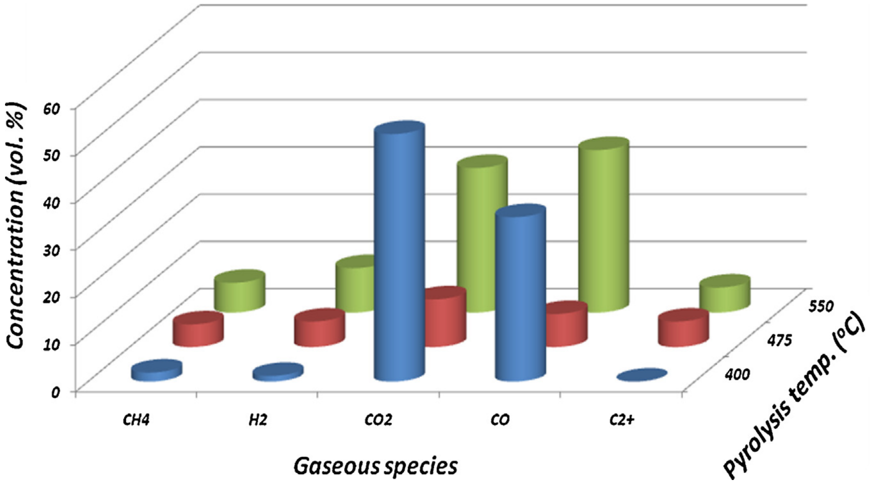

Fig. 7. Composition of gas product obtained from wheat straw at three different pyrolysis temperatures.

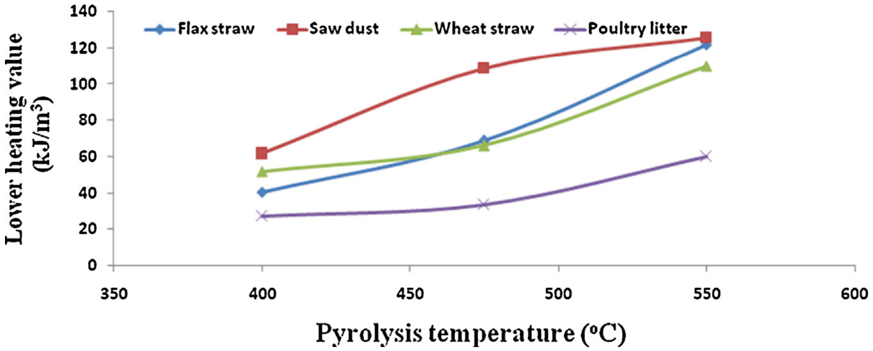

Fig. 8. Lower heating value of gas product collected from pyrolysis unit for different precursors.

4. Conclusions

Efficiency of a mobile pyrolysis unit and effect of pyrolysis temperature were evaluated in terms of physical and chemical properties of the fast pyrolysis products. For all biomass and pyrolysis temperatures, phenolic compounds were the most abundant chemical classes in bio-oil product. Bio-oil showed lower carbon content and larger hydrogen content as compared with those for bio-chars for almost all pyrolysis temperatures. Large content of nitrogen compounds was found in the bio-oil obtained from poultry litter. Ash content of bio-chars was larger at higher pyrolysis temperature. For bio-chars produced from wheat straw and flax straw, the heating value increased by an increase in the pyrolysis temperature. Bio-chars produced from the saw dust showed pH in acidic range (4.4–5.1). LHV for the gas product increased by an increase in pyrolysis temperature. Assessment of pyrolysis products showed that mobile pyrolysis unit can operate for wide range of non-food biomass and its products have great potential for fuel or agricultural applications. In addition, they can be transported to central locations for their conversion to bio-fuels, bio-fertilizers and bio-chemicals.

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